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(54) Fungicidal seed treatment using phosphorous acid or its salts

(57) Seeds and other propagation material, especially monocotyledon plant seeds, are treated with phosphorous acid or a salt thereof as a fungicide.

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Fungicidal seed treatment using phosphorous acid
or its salts.

The present invention relates to the protection of plant seeds and propagation material,
5 including more especially monocotyledon plant seeds, against attacks from fungal diseases, and to compositions useful for this purpose.

It is known that it is possible to control fungal diseases of plants by foliar application of
10 phosphorous acid and its derivatives (Patent GB 1,459,539) but this application has not been used in practice because of the phytotoxicity of compositions containing these ingredients (European Patent Application 230,209).

15 It has now surprisingly been found that it is possible to obtain compositions having a good protective effect on seeds, and plants resulting from the germination of these seeds, by protecting the seeds with phosphorous acid or a derivative thereof, without
20 this protection being disturbed by excessive phytotoxicity.

As used herein, the term "seeds" includes any generative part (propagation material) of the plant which can be used for the reproduction of the latter. This includes not only seed grains (seeds within the narrow meaning), but also roots, rhizomes, fruits, tubers, bulbs, plant parts, germinated plants, young seedlings resulting from any method of propagation from seed grains, cuttings, cell cultures and artificial seeds such as, for example, those described in Patent Applications FR 9305192 or PCT/FR 91/00984 (published under the number WO 92/10087).

The present invention more specifically provides natural or artificial seeds, preferably of monocotyledon plants, and other propagation material comprising, on or inside, as fungicide phosphorous acid or a salt thereof. The presence of another fungicide is not necessary, and in particular the triazole 2-(4-chlorobenzylidene)-5,5-dimethyl-1-(1H-1,2,4-triazol-1-ylmethyl)-1-cyclopentanol (the use of which with a second fungicide which may be inter alia phosphorous acid or a phosphite salt is described in European Specification No. 467792) is not used, but the presence of other fungicides is optional as described below.

Phosphorous acid, also known as phosphonic acid, has the formula H-P(O)(OH)_2 (abbreviated as H_3PO_3). Its salts are known as phosphites, and can be mono- or disalts, preferably alkali metal or ammonium salts, in particular Na_2HPO_3 , K_2HPO_3 or $\text{NH}_4\text{H}_2\text{PO}_3$.

On a practical level, the effective amount of phosphorous acid or salt thereof is generally between 1 g/q and 1 kg/q (q is the abbreviation of quintal = 100 kg), preferably between 5 and 500 g/q.

5 The seed grains are preferably coated in a proportion of 1 to 500 g of active material per quintal of seed grain and preferably 5 to 300 g/quintal. The active material of phosphorous type is preferably chosen such that its solubility in water at 20°C is
10 greater than 0.1 g/l, more preferentially still greater than 0.5 g/l and more preferentially still greater than 50 g/l. Active materials of lower solubility can also be used but it is then necessary to use fairly complicated formulations, for example wettable powders
15 or aqueous suspensions. The use of active materials of sufficiently high solubility as it has just been defined is advantageous in that it makes it possible to treat seeds using simple solutions, which is extremely economic.

20 According to a first variant, the invention further relates to young plants resulting from the germination of the seeds which have just been defined, these young plants being at the one- or two-leaf stage.

 That such young plants are obtained is all
25 the more remarkable since it could be expected that the residual phosphorous acid has a phytotoxic effect with respect to plants resulting from the germination, in the same way that it had a phytotoxic effect in foliar

treatment.

The invention is particularly advantageous in protecting, against fungal diseases, seeds corresponding to crops included in the group comprising
 5 cereals, in particular wheat, barley, rye, winter barley, oats, triticale, maize or rice.

The invention is particularly advantageous in protecting seeds against

* diseases belonging to the group
 10 comprising Pythium arrhenomanes, Pythium graminicola,
Pythium torulosum, Pythium vanterpoolii, Pythium
myriotylum, Pythium periillum, Pythium aristosporum,
Pythium aphanidermatum.

* damping-off,
 15 * root rot,
 * young plant collar rot.

The invention further relates to fungicidal compositions intended for protecting seeds, preferably of monocotyledon plants, against fungal diseases,
 20 characterized in that they contain:

* at least one active material chosen from the group consisting of phosphorous acid or its salts,
 * at least one inert vehicle which is acceptable in agriculture and,
 25 * optionally a surface-active agent which is acceptable in agriculture,
 * the various constituents of these compositions being other than the triazole 2-(4-

chlorobenzylidene)-5,5-dimethyl-1-(1H-1,2,4-triazol-1-ylmethyl)-1-cyclopentanol.

The compositions according to the invention commonly contain between 0.5 and 95% (by weight) of active material of phosphorous type. Preferably, the amount of active material of phosphorous type in these treatment formulations is greater than 5% (by weight).

The present invention also relates to a process for protecting seeds, preferably of monocotyledon plants, against fungal diseases, characterized in that an effective amount of fungicidal active material and/or of fungicidal compositions as defined above is applied to the said seeds. According to this process of the invention, application of the fungicidal active material of phosphorous type is carried out using compositions comprising at least 5% of active material of phosphorous type, preferably at least 10%.

In the present account, the term "vehicle" denotes a natural or synthetic, organic or inorganic material with which the active material is combined to facilitate its application to the seed. This vehicle is thus generally inert and it must be acceptable in agriculture, especially on the treated seed. The vehicle can be solid (clays, natural or synthetic silicates, silica, resins, waxes, solid fertilizers and the like) or, preferably, liquid (water, alcohols, ketones, petroleum fractions, aromatic or paraffinic

hydrocarbons, chlorinated hydrocarbons, and the like).
As has been said above, liquid vehicles are preferred,
in particular those in which the phosphorous active
material is soluble, more especially water and aqueous
5 solutions.

The surface-active agent can be an
emulsifying, dispersing or wetting agent of ionic or
nonionic type. There may be mentioned, for example,
salts of polyacrylic acids, salts of lignosulphonic
10 acids, salts of phenolsulphonic or naphthalenesulphonic
acids, polycondensates of ethylene oxide with fatty
alcohols or with fatty acids or with fatty amines,
substituted phenols (especially alkylphenols or
arylphenols), salts of esters of sulphosuccinic acids,
15 taurine derivatives (especially alkyltaurates), or
phosphoric esters of polyoxyethylenated phenols or
alcohols. The presence of at least one surface-active
agent is often required.

These compositions can also contain any kind
20 of other ingredients such as, for example, protective
colloids, adhesives, thickening agents, thixotropic
agents, penetrating agents, stabilizing agents,
sequestering agents, pigments, dyes or polymers.

More generally, the compositions according to
25 the invention can be combined with all the solid or
liquid additives corresponding to the conventional
formulating techniques for application of seed
treatment in particular.

While on this subject, it will be noted that, in the vocabulary of those skilled in the art, the term seed treatment in fact mainly relates to the treatment of seed grains.

5 The application techniques are well known to those skilled in the art and they can be used without disadvantage in the context of the present invention.

 Mention may be made, for example, of film-coating or coating. Coating is preferred in the
10 invention because of its simplicity; it is sufficient to stir or mix the seed to be treated with the fungicidal compositions according to the invention.

 Among the compositions, solid or liquid compositions may generally be mentioned.

15 There may be mentioned, as forms of liquid compositions or those intended to constitute liquid compositions at the time of application, solutions, in particular water-soluble concentrates, emulsifiable concentrates, emulsions, suspension concentrates or
20 wetttable powders (or powder to be sprayed).

 The emulsifiable or soluble concentrates most often comprise 10 to 80% of active material while emulsions or solutions ready for application contain, for their part, 0.01 to 20% of active material.

25 For example, in addition to the solvent, the emulsifiable concentrates can contain, when this is necessary, 2 to 20% of suitable additives such as stabilizing agents, surface-active agents, penetrating

agents, corrosion inhibitors, dyes or the
abovementioned adhesives.

From these concentrates, it is possible to
obtain, by dilution with water, emulsions of any
5 desired concentration, which are particularly suitable
for application to seeds.

The wettable powders (or powder to be
sprayed) are generally prepared so that they contain 20
to 95% of active material, and they generally contain,
10 in addition to the solid vehicle, from 0 to 5% of a
wetting agent, from 3 to 10% of a dispersing agent and,
when this is necessary, from 0 to 10% of one or more
stabilizing agents and/or other additives, such as
pigments, dyes, penetrating agents, adhesives, anti-
15 clumping agents, and the like.

As has already been said, aqueous dispersions
and emulsions, for example the compositions obtained by
diluting a wettable powder or an emulsifiable
concentrate according to the invention with water, are
20 contained within the general scope of the present
invention. Emulsions can be of the water-in-oil or oil-
in-water type and they can have a thick consistency,
like that of a "mayonnaise".

Among these compositions, a person skilled in
25 the art will advantageously choose that or those which
are suitable depending on the conditions of use.

In the invention, the phosphorous derivative
can be used alone or as a mixture, in particular with

fungicides or insecticides, especially captan, thiram, aspirin or its salts and esters, salicylic acid or its salts and esters, guazatine, oxine-copper, tefluthrin, anthraquinone or metalaxyl, and insecticides such as
5 imidacloprid, lindane and endosulfan, as well as mixtures of these various products.

The following Examples illustrate the invention.

Example 1

10 100 g of barley seed grains were treated with 1.5 ml of an aqueous phosphorous acid or sodium monophosphite (NaH_2PO_3) solution. The concentration of the treatment solution was calculated so as to obtain, on the seed, the dosage (in g/q) of product shown in
15 the Table below. For a dosage of 100 g/q, the concentration of phosphorous acid in the water was 75 g/l.

The treatment was carried out by simple mixing/stirring, for 1 min, so as to obtain seeds
20 comprising various concentrations of phosphorous acid as shown in the Table below.

These seed grains were deposited in pots containing a mixture of peat and pozzolana. One millilitre of Pythium mycelium ground preparation was
25 inoculated into each pot by spraying the earth. There were approximately 20 seed grains per pot.

The seed grains germinated and, 15 days after sowing, the state of the plants was observed with

respect to control seed grains not treated with phosphorous acid and with respect to control seed grains not inoculated with Pythium. All the plants which had survived had two leaves. No phytotoxicity was
 5 observed in any case.

The results were the following:

Fungicidal agent	Dose in g/q	Efficiency expressed as percentage *	
		<u>Pythium arrhenomanes</u>	<u>Pythium myriotylum</u>
Phosphorous acid	50	60	40
	100	100	60
Sodium monophosphite	100	75	20
	200	100	70
	400	100	100
	800	100	100
Untreated control inoculated with <u>Pythium</u>	0	0	0

*i.e. the number of surviving treated seedlings expressed as a percentage of the number of surviving seedlings which had received neither the fungicidal
 15 agent nor the inoculation with Pythium.
 20

Example 2

Barley seed grains were treated, as in Example 1, with aqueous dipotassium phosphite solution. To obtain a dosage of 240 g/q of product on the seeds, 100 g of seeds were treated with 1.5 ml of a solution
5 containing 80 g/l of K_2HPO_3 .

The seed grains thus treated were sown in an open field and the state of the crop was observed 72 days after sowing with respect to an untreated control.

Both crops were affected by fungal attacks
10 of Pythium arrhenomanes. As compared with the untreated plants, the plants treated according to the invention contained 2.8 times more roots and were greater in number by 24.3%. The weight of dry matter of the roots of the treated plants compared with the
15 untreated plants was greater by 39%.

CLAIMS

1. Plant seeds, and other propagation material, comprising as fungicide phosphorous acid or a salt thereof.
- 5 2. Plant seeds according to claim 1 which are monocotyledonous.
3. Seeds according to claim 2 which are cereal seeds, in particular of wheat, barley, rye, winter barley, oats, triticale, maize or rice.
- 10 4. Seeds according to claim 1, 2 or 3 which comprise phosphorous acid or an alkali metal or ammonium salt thereof.
5. Seeds according to claim 1, 2 or 3 which comprise a phosphorous acid salt having a solubility in
15 water at 20°C greater than 0.1 g/l, preferably greater than 0.5 g/l.
6. Seeds according to any one of claims 1 to 5, which comprise from 1 g/q to 1 kg/q, and preferably from 5 to 500 g/q, of the phosphorous acid or salt
20 thereof.
7. Seeds according to any one of claims 1 to 6, which also comprise a second active material chosen from captan, thiram, guazatine, oxine-copper, metalaxyl, imidacloprid, lindane and endosulfan.
- 25 8. Seeds according to any one of claims 1 to 6, which also comprise a second active material chosen from aspirin, its salts and esters and salicylic acid and its salts and esters.

9. Method for protecting seeds and other propagation material, preferably of monocotyledon plants, against fungal diseases, which comprises applying thereto an effective amount of phosphorous acid or a salt thereof.
10. Method according to claim 9 wherein the fungal disease is
- * a disease caused by Pythium arrhenomanes, Pythium graminicola, Pythium torulosum, Pythium vanterpoolii, Pythium myriotylum, Pythium periillum, Pythium aristosporum, or Pythium aphanidermatum
 - * damping-off,
 - * root rot, or
 - * young plant collar rot.
11. Young plants, resulting from the germination of seed according to any one of claims 1 to 8 or treated by the method of claim 9 or 10 .
12. Fungicidal composition useful for protecting seeds and other propagation material comprising, as fungicide,
- * at least one active material chosen from phosphorous acid and its salts,
 - * at least one inert vehicle which is acceptable in agriculture, and
 - * a surface-active agent which is acceptable in agriculture.
13. Composition according to claim 12, which

contains between 0.5 and 95% of the said active material.

14. Composition according to claim 12 or 13, wherein the inert vehicle is liquid, preferably water.

Relevant Technical Fields

- (i) UK Cl (Ed.M) ASE (EAB, EN)
(ii) Int Cl (Ed.5) A01N 59/26

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES: WPI

Search Examiner
P N DAVEY

Date of completion of Search
1 AUGUST 1994

Documents considered relevant
following a search in respect of
Claims :-
1-14

Categories of documents

- X:** Document indicating lack of novelty or of inventive step. **P:** Document published on or after the declared priority date but before the filing date of the present application.
- Y:** Document indicating lack of inventive step if combined with one or more other documents of the same category. **E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.
- A:** Document indicating technological background and/or state of the art. **&:** Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X	GB 1459539	(PHILAGRO) see especially examples	1, 4, 9, 11, 12 and 14 at least
X	EP 0540300 A1	(RHONE-POULENC) see for example Claim 16	12-14
X	EP 0467792 A1	(RHONE-POULENC) see for example Claims 11 and 18	1-4, 9, 11, 12 and 14 at least
X	EP 0230209 A2	(CIBA GEIGY) see for example pages 12-13	12-14

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).